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Chemical Analysis of Stationary Source Particulate Pollutants by Micro-Raman Spectroscopy

Interim Report

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Analytical capability to identify the principal molecular species present in microparticles is demonstrated on the basis of Raman spectra of selected compounds and materials. Among the inorganic species studied are sulfates, nitrates, carbonates and oxides, for which Raman spectra are discussed for single, solid particles of size down to 1 micrometer. The method of micro-Raman analysis is applied to the molecular characterization of individual microparticles from power plant emissions. Raman spectra have been obtained from microparticles of oil-fired power plant emissions collected by the EPA with cascade impaction samplers.

Vanadium pentoxide, V_2O_5, has been identified as a major component of microparticles present in such samples. The presence of certain other vanadium containing species such as vanadyl, VO^{2+}, and ortho-vanadate, VO_4^{3-}, is not indicated from the results of these measurements. Other Raman spectra show evidence of crystalline sulfate, SO_4^{2-}, as a species present in major proportions. However, the exact nature of the associated cation specie(s) has not been determined. Many of the spectra obtained from fly ash particles show Raman bands characteristic of polycrystalline graphite apparently due to the presence of carbonaceous material associated with the particles.

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Interim Report

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PREFACE

The ability to determine the chemical species composition of individual microparticles is of major importance to the study of the origins and transformations of particulate matter. This is especially true for the analysis of particles emitted by stationary sources, such as oil-fired and coal-fired power plants. The NBS micro-Raman spectrometer is a unique instrument that can be applied to the solution of problems dealing with the chemical species characterization of stationary source particulates. This report gives the results of a preliminary study of the application of the micro-Raman technique to power plant particulate emissions.

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ABSTRACT

The application of laser-Raman spectroscopy to the molecular characterization of individual particulates from stationary sources is described. This research was performed using the NBS-developed Raman microprobe. Analytical capability to identify the principal molecular species present in microparticles is demonstrated on the basis of Raman spectra of selected compounds and materials. Among the inorganic species studied are sulfates, nitrates, carbonates and oxides, for which Raman spectra are discussed for single, solid particles of size down to 1 micrometer. Preliminary results on liquid sulfate particles generated from sulfuric acid aerosol are presented. The method of micro-Raman analysis is applied to the characterization of microparticles from power plant emissions. Raman spectra have been obtained from microparticles of oil-fired power plant emissions collected by the EPA with cascade impaction samplers.

Vanadium pentoxide, V_2O_5, has been identified as a major component of microparticles present in such samples. The presence of certain other vanadium containing species such as vanadyl, VO^{2+}, and ortho-vanadate, VO_4^{3-}) is not indicated from the results of these measurements. Other Raman spectra show evidence of crystalline sulfate, SO_4^{2-}, as a species present in major proportions. However, the exact nature of the associated cation specie(s) has not been determined. Many of the spectra obtained from fly ash particles show Raman bands characteristic of polycrystalline graphite. These carbon bands appear to derive, in the majority of cases, from the presence of carbonaceous material associated with the particles. The need for further work is indicated from these exploratory measurements. Recommendations are made as to the scope and direction for this work.

This report was submitted in fulfillment of Contract No. EPA-IAG-D6-F012 by the Analytical Chemistry Division, National Bureau of Standards, under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period April 1, 1976, to March 31, 1977, and work was completed as of March 31, 1977.

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SECTION 1

INTRODUCTION

This report under EPA-IAG-D6-F012 agreement summarizes the work performed for the period April 1976 through March 1977. The purpose of the project is to investigate the application of Raman spectroscopy to the analysis of the molecular composition of single, micrometer-size particles in particulate matter from stationary sources. The scope of this work is to entail activities in the following principal areas:

1. The partial automation of the NBS micro-Raman spectrometer system to permit the rapid sequential analysis of multi-particle samples.

2. The acquisition of particle reference spectra of various major types of stationary source particulates of interest to the EPA, including sulfates, nitrates and carbonates.

3. The Raman spectroscopic analysis of several representative particulate samples provided by the EPA. These samples should have been previously characterized for elemental composition by the EPA to provide a basis for comparison with the micro-Raman results.

4. Cooperation with the EPA in the development of stack sampling methods compatible with the sample requirements of micro-Raman analysis and consultation in the area of Raman and fluorescence spectroscopy.

The research conducted under this work agreement addresses itself to questions concerning the chemical species and the crystalline or glassy state of particles. A major goal of the project is to demonstrate the potential of the micro-Raman spectroscopy technique for the molecular analysis of major constituents in particles from stationary sources, with emphasis on those from the combustion of fossil fuels.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The results presented in this report demonstrate the potential of micro-Raman analysis for the chemical characterization of fine particulates. The study of single microparticles of well-characterized materials has established the capabilities and limitations of the present configuration of the Raman microprobe. Individual particles down to 1 μm in size can routinely be analyzed with the instrument. In these measurements good detectability is achieved for the major types of inorganic species suspected to occur in the environment in microparticulate form. These include the common oxides, carbonates, nitrates, sulfates, and phosphates as well as a variety of the terrestrial minerals. In addition, several classes of organic compounds and polymers have been characterized by the micro-Raman technique.

The analysis of small particles is most straightforward when they are transparent to the exciting radiation. Radiation absorbing, colored particles may heat as a result of the interaction with the focused beam and give rise to irreversible modification of the sample.

Important to the success of the Raman characterization of unknown particles is the availability of particle reference spectra obtained from the measurement of well-characterized source materials. A major effort that has been expended as part of this work and which will extend into the future does center on the acquisition of a reference spectra file for microparticle analysis.

Vanadium pentoxide, V_2O_5, has been identified as a major component of microparticles present in oil-fired power plant samples. The presence of other vanadium containing species (e.g., vanadyl, VO^{2+}, and ortho-vanadate, VO_4^{3-}) is not indicated from the results of these measurements. Other Raman spectra show evidence of crystalline sulfate, SO_4^{2-}, as a species present in major proportions. However, the exact nature of the associated cation specie(s) has not been determined. Many of the spectra obtained from fly ash particles show Raman bands characteristic of polycrystalline graphite. These carbon bands appear to derive, in the majority of cases, from the presence of carbonaceous material associated with the particles.

As has been demonstrated in these measurements, spectra are obtained that can be correlated with the presence of major constituents when appropriate reference spectra are available. In cases where particle identification based on the Raman spectrum is not possible, the application of other microanalytical methods must be sought to achieve the desired result. To date we have not explored the full analytical potential of combining the micro-Raman technique with other methods of particle microanalysis. Identification of an unfamiliar Raman spectrum is made easier if the elemental composition of the sample is known.

The preliminary results obtained from the micro-Raman analysis of particles in power plant emissions indicate that further research is required to characterize such samples. Several problems are perceived that need to be examined in future work. Among these is the collection of such samples for micro-Raman analysis. Bulk particulate samples collected on filters or other supports are least suited for single particle characterization. They require the isolation of particles by methods that do not alter the integrity of the particle. The measurement is frequently difficult due to the presence of contaminants introduced by the method of sampling and through inter-particle contact. The bulk sampling of particulates provides ample opportunity for reactions to take place that change the morphology and chemical nature of microparticles. These events tend to complicate the spectrochemical information derived from such samples and frequently place into question the original identity of the particle under study. The collection of suspended particles by impaction on the Raman substrate offers the opportunity for unambiguous sampling of the aerosol. When on-site sampling conditions are optimized, the sample consists of a deposit of particles of sufficiently low particle density to exclude the possibility of significant particle modification due to inter-particle reactions. It is also clear from our analyses of unknown particles that greater emphasis must be placed on the application of analytical methods that combine the micro-Raman technique with other micro-analytical probe techniques (e.g. electron probe and ion probe micro-analysis).

We propose a continuation of the project which should have as its objective the detailed Raman investigation of power plant particulate emissions collected on micro-Raman substrates. These studies should seek to optimize the sample collection from these sources and include in-stack and out-of-stack sampling of the aerosol. For these investigations to be of greatest utility, it is suggested that any further work in this area on the part of NBS be closely coordinated with the parallel efforts underway at the EPA in the characterization of such samples by other methods.

SECTION 3

PARTICLE ANALYSIS BY RAMAN SPECTROSCOPY

The application of Raman spectroscopy to the analysis of small, single particles yields chemical information on such samples which cannot be obtained by other microanalytical techniques (e.g., electron probe and ion probe microanalysis). For a broad range of both inorganic and organic compounds the technique has the potential of furnishing not only the structural formula of the molecular species contained in the particle, but in addition may yield information on the long-range molecular order (i.e., crystalline or glassy state) of the material. The Raman spectrum that is obtained from such microscopic samples will therefore, in many cases, represent a unique "fingerprint" of the constituent chemical species and their structural coordination. The technique can readily distinguish, for example, between sulfate, SO_4^{2-}, sulfite, SO_3^{2-}, either of the corresponding protonated forms, HSO_4^- or HSO_3^-, and sulfide, S^{2-}, in a respirable-size particle when these species are a major constituent. Moreover, the Raman spectrum is sufficiently different for distinguishing among the various crystalline forms of calcium sulfate, i.e. gypsum ($CaSO_4 \cdot 2H_2O$), hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$), and soluble and natural anhydrite ($CaSO_4$).

The analysis of molecular ions (such as SO_4^{2-}, other oxyanions of sulfur, NO_3^-, etc.) in the atmospheric environment is an area of intense interest and the focus of many current investigations. Of primary importance is an increased understanding of the atmospheric chemistry leading to the formation of "acid aerosol" from sulfur dioxide, SO_2. This requires determining the specific chemical nature of atmospheric aerosol and frequently a correlation of particle composition with particle size. These species, including atmospheric H_2SO_4 present as droplets of the free acid and the half-neutralized acid, NH_4HSO_4, have to this date proved difficult to identify by traditional air sampling methods followed by ionic analyses (i.e. wet chemical methods) of bulk samples or used in conjunction with microchemical tests for individual species contained in single, microscopic particles.

REQUIREMENTS FOR MICRO-RAMAN ANALYSIS

The development of the new Raman microprobe was preceded by earlier work [1] at NBS in which it was demonstrated that the Raman spectrum could be obtained from single, micrometer-size particles. These results showed that the Raman frequency and line shape are not affected (from analytical considerations) by the fact that the molecules of the sample make up a small particle. It was concluded that the spectra are essentially the same as those observed from bulk quantities of the material and could provide a basis for the chemical identification of small particles present in many forms of particulate matter.

We have discussed in earlier published work [1,2] the experimental requirements that must be met to permit the recording of the Raman spectrum from microparticles of size down to 1 μ. These criteria are, high spectral sensitivity to extremely low signal levels, effective rejection of optical interferences, and appropriate choice of irradiance (power per unit area) levels placed in a focused laser beam that will not bring about modification or destruction of the sample by heating or photodecomposition.

The new Raman microprobe developed at the NBS has been constructed to meet these requirements for single particle analysis. A description of the design of the instrument and a discussion of its optical and mechanical performance has been presented in a recent publication [2]. This paper also presents the results of measurements performed to demonstrate the broad capabilities of the micro-Raman spectroscopy technique in several areas of application.

SECTION 4

COMPUTERIZATION OF THE MICRO-RAMAN SPECTROMETER SYSTEM

MODIFICATIONS OF INSTRUMENT DESIGN

A complete description of the overall design and configuration of the Raman microprobe is given in the recent literature [2]. Some modifications have been made in the design of the instrument to optimize its performance in the application to the analysis of environmental particulates contained in multi-particle samples.

Fore Optical System

Initially, a reflecting objective (Beck, 15X, N.A. 0.28) was chosen to focus the exciting laser beam to a diffraction-limited beam spot of approximate diameter 2 μm. Because of the design of the Beck objective (which yields a classical, non-Gaussian beam) the irradiance placed on the sample could only be reduced below its maximum value by approximately a factor of 20, - the limit which is imposed by the stable operating range of the laser. In order to measure absorbing samples, it is frequently necessary to vary the irradiance by an additional order of magnitude (i.e., a total range factor of approximately 200). This is accomplished most effectively by varying the spot size of the focused beam, which is not possible with the Beck objective. To extend the application of the instrument to the routine analysis of radiation absorbing, temperature sensitive materials, the Beck objective was replaced with a refractive objective lens (Leitz, 5.6X, N.A. ∿0.15) which allows measurements at reduced irradiance levels. The power throughput for this lens is approximately 2.5 times that of the Beck and it furnishes a minimum spot diameter of ∿7 μm. Thus, the maximum irradiance is about one-fourth of that available from the Beck and is adequate for most routine measurements of single particles of size down to 2-3 μm. For larger particles, the use of the focused beam of lower irradiance results in essentially no loss in signal compared to signal levels obtained with the Beck.

Sample Stage Translation

To fully automate the spectroscopic analysis of multi-particle samples new sample translation devices needed to be incorporated into the design of the sample stage. These modifications involved the installation of piezoelectric "inchworm" translators (Burleigh Instruments, Inc., Model PZ500) to drive the sample stage in the x/y plane. These devices provide high resolution travel (single step resolution as fine as 0.01 μm) over a distance of 25 mm.

They are replacing the more conventional differential screw micrometers used to translate the sample stage in the earlier configuration of the system.

The new inchworm translators are driven by an external controller (Burleigh, Model PZ-502) which is interfaced by the computer allowing for pre-programmed stepping of the stage.

Spectrometer Computer Interface and Software Development

The micro-Raman spectrometer system has been designed to be interfaced to a dedicated mini-computer to permit automation of the measurements and optimized, automatic data acquisition.

The interface of the Nova 1200 computer to the spectrometer system is a modified Digilab system. Each of its functions have been tested and are now operative. The interface provides the capability to read the digital output of the two-channel photon counter into the computer and will replace the present analog, strip-chart recording system. This allows background-corrected and intensity-normalized spectra to be obtained. In addition, the interface permits computer control of the photon counter count time, the setting of the spectrometer slits, stepping of the wavelength scan, and translation of the sample stage. Full integration and testing of the operating system is continuing. Significant improvement in the acquisition and manipulation of spectral data will result from the computerization of the system.

SECTION 5

REFERENCE SPECTRA FOR MICRO-PARTICLE RAMAN ANALYSIS

In the following are discussed selected examples of both inorganic and organic compounds characterized as single particles by application of the Raman microprobe. These materials are of interest since they are expected to be present in stationary source emissions from fossil fuel power plants.

INORGANIC COMPOUNDS AND MINERALS

Sulfates/Sulfites

Simple (e.g., Na_2SO_4) and complex (e.g., $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) sulfate salts have been studied as model compounds for the Raman characterization of crystalline sulfate in airborne particles. Typical of these measurements are the spectra shown in Figure 1 and Figure 2. These and all other spectra discussed exhibit approximately the same format. The frequency shifts in wavenumber units for the Stokes-Raman scattering are displayed on the horizontal axis. Plotted along the vertical axis is the value of the scattered light intensity in photon counts observed in a measurement time referred to as the time constant. The zero of light intensity is indicated by the solid horizontal base line. In some examples, the Raman shifts characteristic of the particle are indicated by markers labeled "P" and the bands associated with the sapphire substrate are marked "S". All spectra have been recorded at room temperature with an effective resolution of approximately 3 cm^{-1}. Frequency calibrations were obtained by recording the neon and argon emission lines, providing an accuracy of ± 3 cm^{-1}. The spectra of the sulfates are discussed in some detail to indicate the specificity of the Raman method for qualitative identification. In each case, the band assignments made are those reported in the literature.

As in the bulk (i.e., as single crystals), microparticles of sulfate salts and sulfate minerals give very strong and sharp Raman spectra. These have been reviewed, along with the vibrational spectra (IR data included) of other classes of inorganic compounds and minerals, in the recent literature [3,4]. Theory predicts four fundamental Raman-active modes of the undistorted, free SO_4^{2-} ion of tetrahedral symmetry. In the crystalline state, the number and frequency positions of the vibrational modes associated with the SO_4^{2-} ion will depend on the number of ions in the unit cell (primitive) and the local symmetry about the SO_4^{2-} ion. Most characteristic of the solid sulfates is the strong, symmetric stretch (ν_1) near 1000 cm^{-1}. In the sulfates we have examined, this is a single, sharp line. The other fundamental modes are of weaker intensity and are resolved as either doublets or triplets in the spectra of the sulfate microparticles. The spectrum in Figure 1 of a microparticle

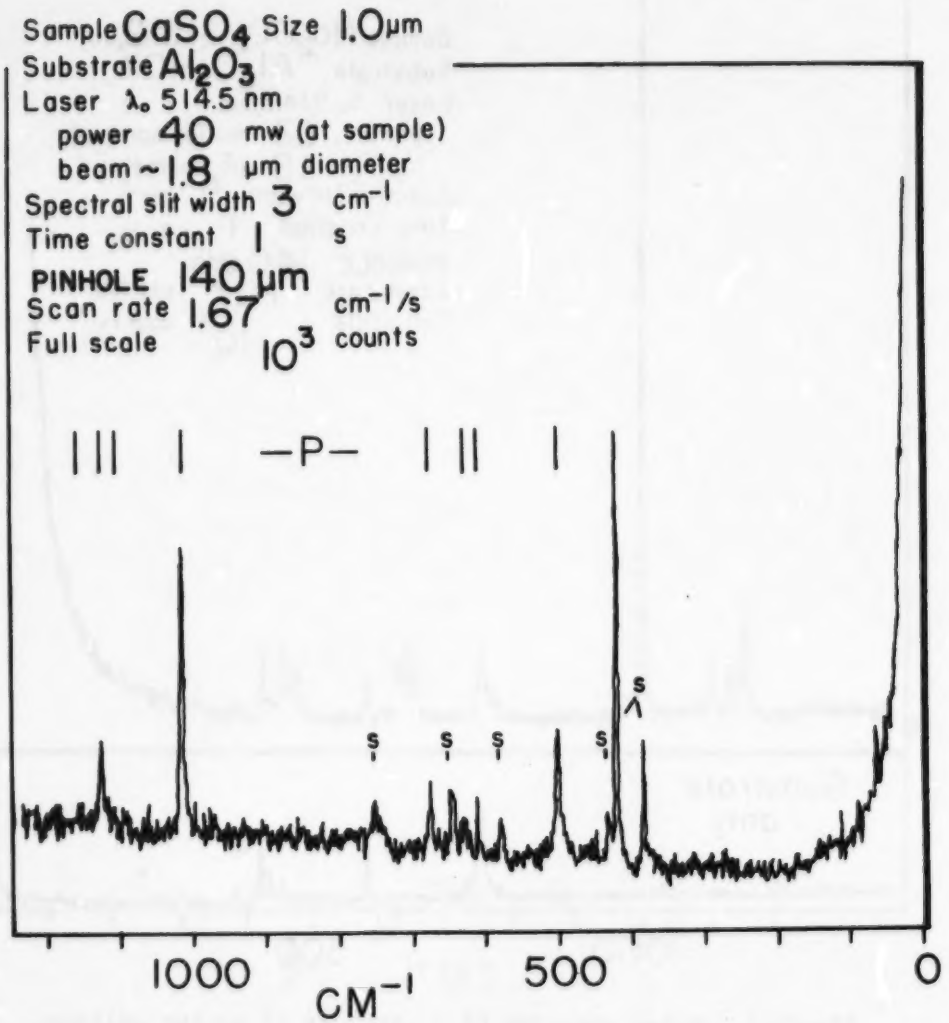


Figure 1. Raman spectrum of a particle of anhydrite.

of anhydrite ($CaSO_4$) shows many of the expected modes - marked "P" - characteristic of the internal vibrations of the sulfate group in the crystal. The bands marked "S" are most of the expected modes of sapphire and appear in the spectrum at 378, 418, 432, 451, 578, 645 and 751 cm^{-1}. Analysis shows there are nine Raman-active internal modes of the SO_4^{2-} ion in $CaSO_4$.

Spectra of similar quality have been obtained from microparticles of Na_2SO_4 in sizes down to 2 μm. The spectrum in Figure 2 is representative of these results. In this measurement, the hygroscopic particle is encapsulated by a thin film of low fluorescence immersion oil to prevent its modification by moisture in the air. Raman data have been reported for this salt and the

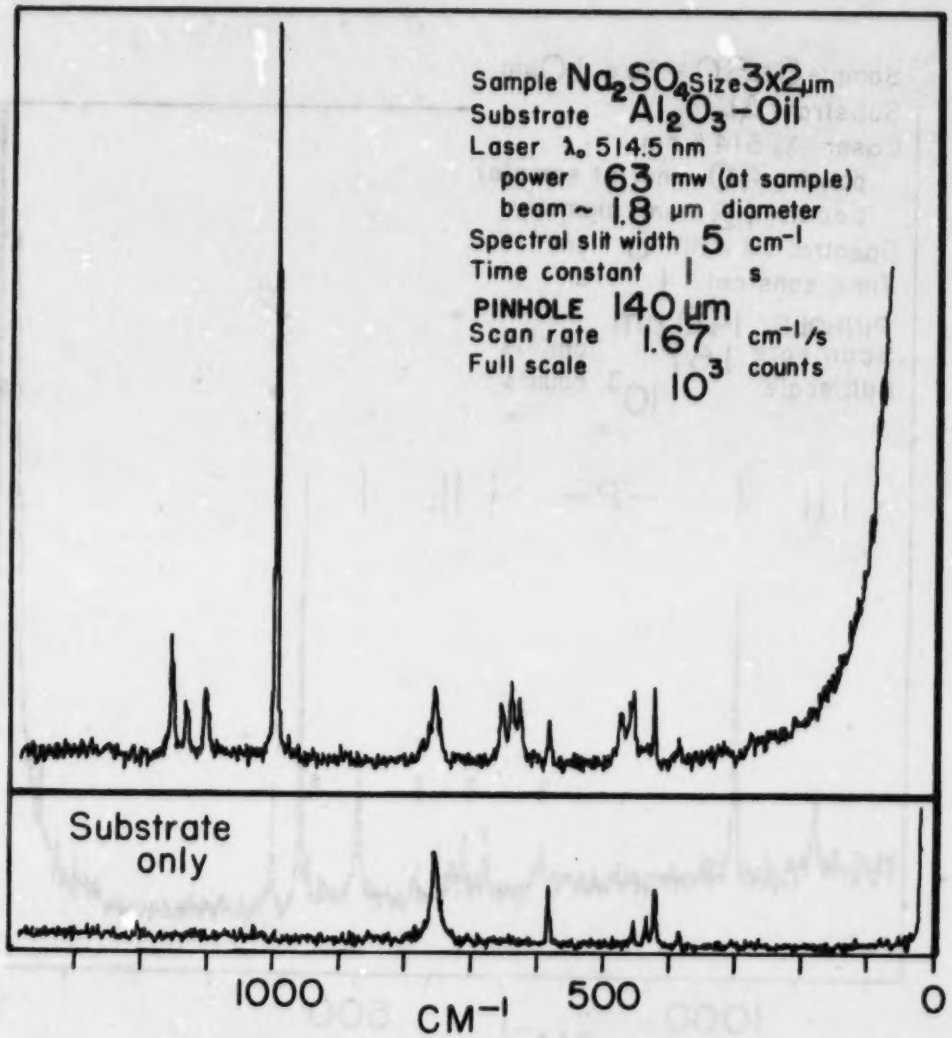


Figure 2. Raman spectrum of a particle of sodium sulfate.

bands observed in the spectrum of the particle (c.f. Table 1) are consistent with the literature values. Included also in Figure 2 is the spectrum of the substrate (i.e., sapphire), recorded by simply moving the particle out of the focal spot of the beam. A third example is the spectrum of a small particle of $(NH_4)_2SO_4$ (c.f. Figure 4 of Ref. 2.) The internal modes of the NH_4^+ ion in this salt have been reported to be centered around 3124 cm^{-1} (ν_1), 1669 cm^{-1}(ν_2), 3137 cm^{-1} (ν_3), and 1429 cm^{-1} (ν_4). Of these the bending modes appëar in the spectrum of the particle as broad features around 1670 cm^{-2} and 1430 cm^{-1}. Each mode of the NH_4^+ ion is broader than the corresponding one of the SO_4^{2-} ion. The various bands observed below 400 cm^{-1} arise from external modes of the crystal. The strong band at ~73 cm^{-1} has been assigned to a translatory mode of the SO_4^{2-} ion. The weaker bands in the

region 150-210 cm^{-1} are attributed to translatory modes of the NH_4^+ ion. The spectra presented in these figures show good signal-to-noise for the fundamental sulfate modes in these microcrystals. High irradiance levels were placed on the microsample in each measurement without adverse effects on the particle. Spectra of similar quality were recorded from microparticles of other common sulfates (e.g., Na_2SO_4, $PbSO_4$) and double salts containing sulfate (e.g., $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$).

The Raman shifts observed from microparticles of several common crystalline sulfates are given in Table 1. Comparison of the frequencies for the sulfate ion in anhydrite and in gypsum, $CaSO_4 \cdot 2H_2O$, shows that the hydrated and non-hydrated forms can readily be distinguished.

The selected data presented in the table indicate the ability to spectroscopically discriminate among the various crystalline sulfates in microparticles. Raman data of this kind are available in the literature for many inorganic compounds and minerals. The Raman shifts given for the free SO_4^{2-} ion correspond to the frequencies of the fundamental modes of the ion in solution. The half-widths of Raman lines of dissolved species are generally broader, and the bands are less intense (concentration effect) than in the solid phase. These observations are relevant to the micro-Raman characterization of liquid microparticles, as will be shown.

TABLE 1. INTERNAL VIBRATIONAL MODES OF THE SULFATE ION IN FOUR COMMON CRYSTALLINE SULFATES MEASURED IN THE RAMAN MICROPROBE

Compound	SO_4^{2-} Frequency Shift, cm^{-1}			
	ν_1 symm. stretch	ν_2 symm. bend	ν_3 asymm. stretch	ν_4 asymm. bend
Na_2SO_4	997	472,455	1162,1135,1110	661,640,628
$(NH_4)_2SO_4$	976	452,447	1062,1075,1089	617,612
$CaSO_4$	1018	497,418	1060,1128,1108	674,628,608
$CaSO_4 \cdot 2H_2O$	1006	493,413	1142,1135,1116	670,623
Free SO_4^{2-} ion	981	451	1104	613

Sulfamic acid (amidosulfonic acid) H_2NSO_3H, has been studied in the Raman microprobe. With this material the primary interest lies in the spectroscopy of the SO_3^{2-} grouping as compared to that of the SO_4^{2-} grouping in solid sulfates. The acid is suspected to be an important constituent of continental aerosols, or precursor to atmospheric ammonium sulfate particles. Parallel interests center on the spectroscopic characterization of other crystalline materials containing the sulfite, SO_3^{2-} and bisulfite, HSO_3^-, species; this in

view of the toxicological importance of tetravalent sulfur in respirable particulates and the significance of heavy metal-sulfite complexes in the atmospheric environment. Preliminary results indicate good detectability for the common (i.e., Na^+, NH_4^+ salts) sulfites down to particle sizes of a few micrometers.

Phosphates

Phosphates give very strong, sharp Raman spectra. Similar spectroscopic arguments exist for the phosphate grouping, PO_4^{3-}, as have been presented for the SO_4^{2-} anion in crystalline solids. The ν_1 symmetric stretch of the phosphate ion is normally the strongest and sharpest band in the spectrum and often a good guide to identification.

Micro-Raman measurements have been made on a well-characterized sample of calcium fluorapatite, $Ca_5(PO_4)_3F$. Excellent Raman spectra have been obtained for single particles down to 2-3 μm in size. These spectra show one-to-one correspondence with the Raman data reported for bulk samples.

Figure 3 shows a typical spectrum, obtained from a small particle of calcium fluorapatite. Since there are two PO_4^{3-} groups in the unit cell, theory predicts 15 Raman-active internal modes, most of which are resolved in the

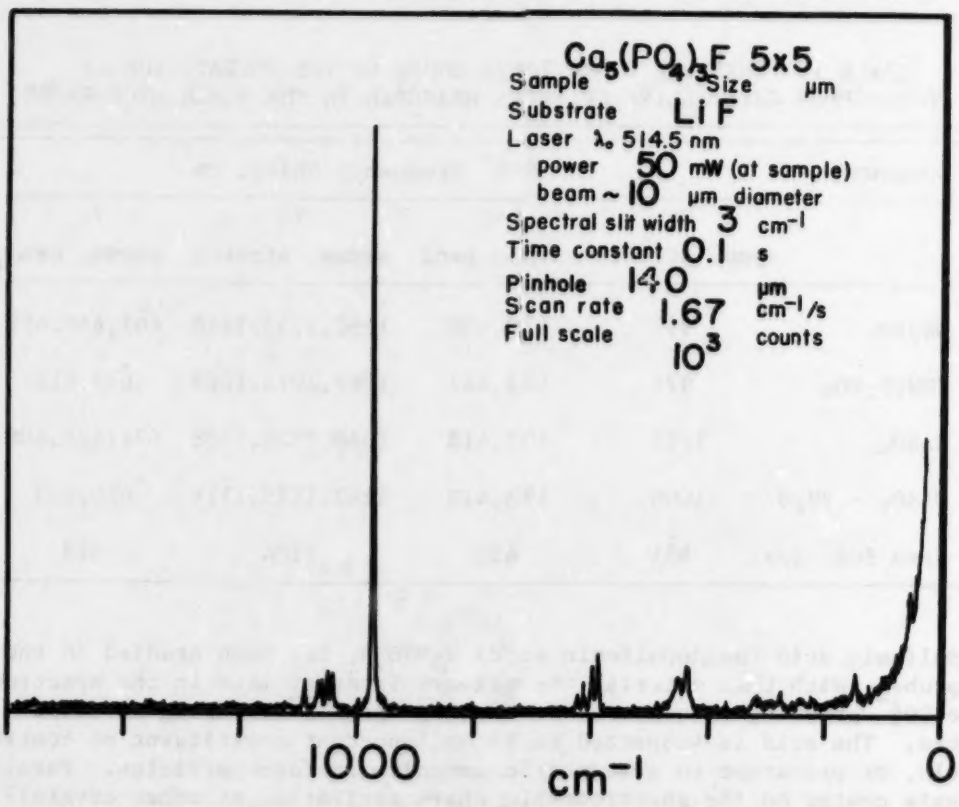


Figure 3. Raman spectrum of a particle of calcium fluorapatite.

spectrum of the microparticle. The multi-component bands arising from these modes are of much weaker intensity than the ν_1 symmetric stretch observed at 965 cm^{-1}. These split fundamentals are centered around 430 cm^{-1} (ν_2), 600 cm^{-1} (ν_4) and 1050 cm^{-1} (ν_3). These results indicate spectroscopic detectability for mineralogical phosphates in particles of size down to one micrometer.

Carbonates

Microparticles of single-crystal calcite, $CaCO_3$, have been studied in the Raman microprobe in order to establish detectability of microcrystalline calcite. Good spectra were obtained for single particles approaching 1 μm in linear dimensions. A representative result is the particle spectrum of calcite shown in Figure 4. Parallel measurements performed on micrometer-size particles of chicken eggshell (i.e., $CaCO_3$) have yielded spectra consistent with that shown in Figure 4.

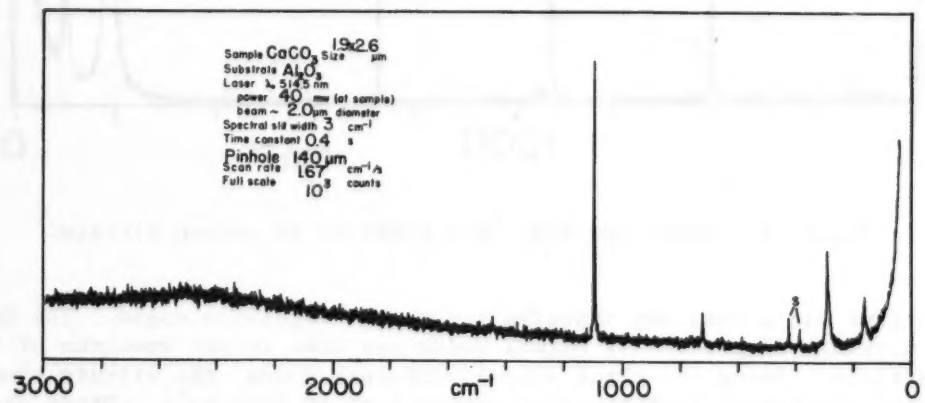


Figure 4. Raman spectrum of a particle of calcite.

Carbonates in general are recognized by the appearance of the strong symmetric stretch ν_1 near 1100 cm^{-1}. For calcite, this internal vibrational mode has shift 1088 cm^{-1}. The asymmetric stretch ν_3 of the CO_3^{2-} anion is predicted at 1432 cm^{-1} and is barely resolved in the spectrum of the microparticle, in part due to the moderately high background signal level in this spectral region. The asymmetric bend ν_4 appears with Raman shift 714 cm^{-1}, and the expected lattice (external) vibrations are seen at 283 cm^{-1} and 156 cm^{-1}. The symmetric bend ν_2 of the carbonate ion is Raman-inactive for solids of the calcite structure.

Nitrates

Several nitrates have been characterized as microparticles. The spectrum, shown in Figure 5, of a small particle of single crystal $NaNO_3$, is typical of these results. Sodium nitrate has the calcite ($CaCO_3$) structure and five

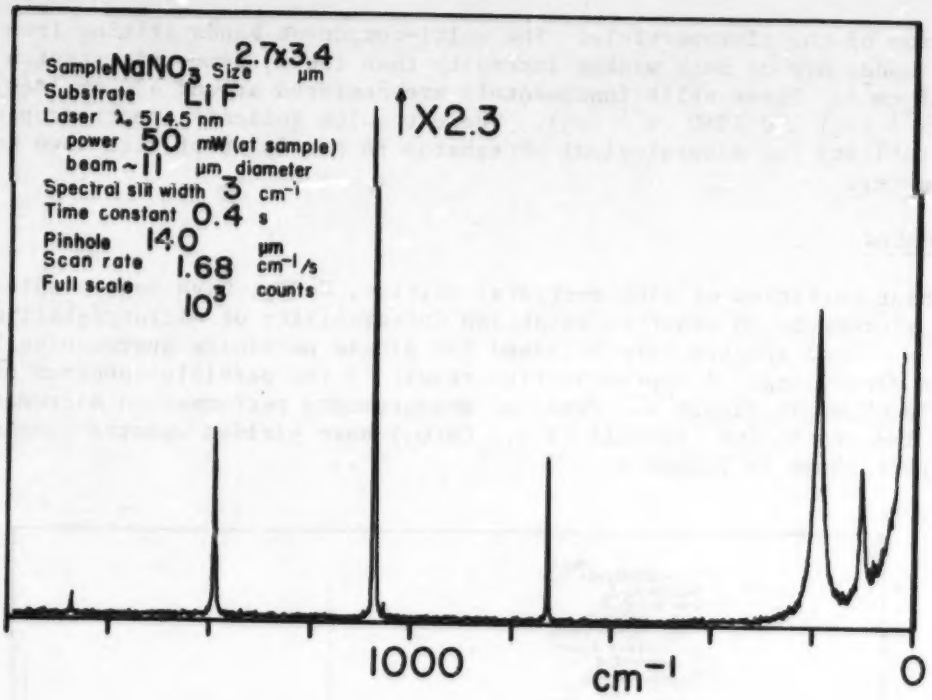


Figure 5. Raman spectrum of a particle of sodium nitrate.

Raman-active vibrations are expected for this crystalline solid. The frequency shifts corresponding to these normal modes are seen in the spectrum of the microparticle. Among the three allowed internal modes, the nitrate symmetric stretch ν_1 gives rise to the strong, sharp band at 1068 cm^{-1}. Other characteristic lines have shifts 1385, 724, 185 and 98 cm^{-1}, where the latter two represent the expected lattice vibrations. These values are consistent with those given in the literature. The position of these bands in the alkali-metal nitrates is sensitive to the associated cation and the crystalline structure of the solid. In the case of KNO_3, for example — because of the higher mass of the cation — the two corresponding lattice modes are shifted appreciably (by $\sim$55 cm^{-1}) toward lower frequencies. The nitrate symmetric stretch ν_1 in crystalline KNO_3 falls at 1048 cm^{-1} and is equally strong in intensity. The $NaNO_3$ particle in the spectrum of Figure 5, it is noted, is supported by a LiF substrate. There is no first-order scattering from this material and background levels are seen to be extremely low in the absence of any broad band fluorescence from these substrates.

Microparticles of NH_4NO_3 and $Pb(NO_3)_2$ have also been measured in the microprobe furnishing good spectra useful for reference purposes.

These nitrates are very strong Raman scatterers and can routinely be detected and identified in particles of size down to 1 μm. Since some of these salts are hygroscopic, measurement difficulties have been encountered when ambient humidities are high and as a result the nitrate microparticles are

modified due to adsorption of atmospheric moisture. Under these conditions, spectral lines tend to broaden and Raman intensities fall off considerably. This may be associated with changes in particle morphology or surface related effects.

Oxides and Hydroxides

Particle Raman spectra have been obtained for several selected oxides and hydroxides. Thorium oxide, ThO_2, has been of particular interest on account of its refractory properties (m.p. 3050 °C) and the exceptional simplicity of its vibrational Raman spectrum. The spectrum of a 0.8 μm particle of ThO_2 is shown in Figure 3 of Reference 2.

Other oxides characterized include crystalline quartz (α-SiO_2) and alumina (α-Al_2O_3), i.e., sapphire, the latter because of its use as a substrate. Microparticles prepared from crushed, single-crystal, natural quartz have been measured to locate the expected Raman frequencies in the spectrum. Figure 6 of this report shows the spectrum of an "unknown" particle of respirable size found in a bulk sample of urban air particulate dust. The particle is identified as crystalline quartz.

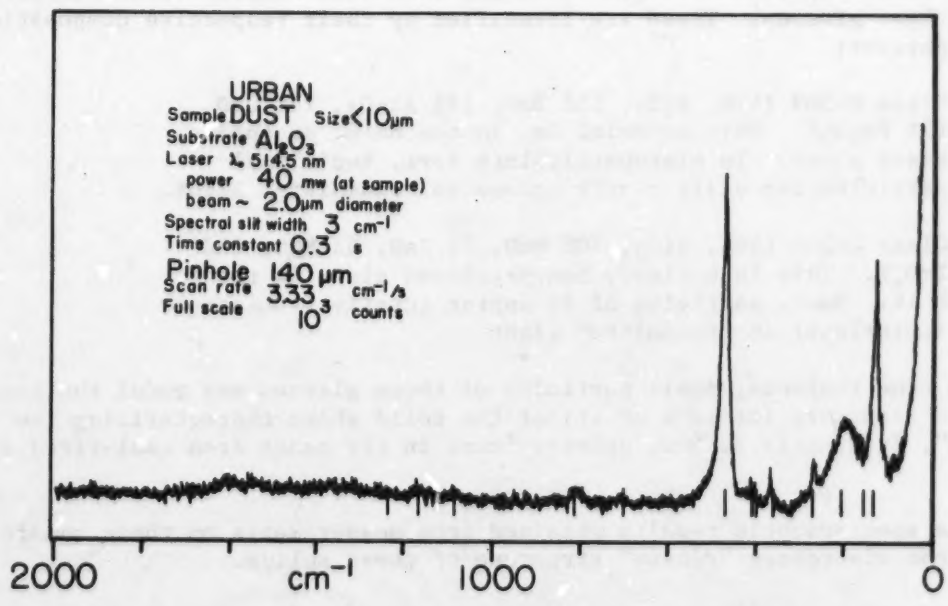


Figure 6. Raman spectrum of a particle of crystalline quartz (α-SiO_2) in urban air particulate dust.

Compared to quartz, sapphire or the mineral corundum (α-Al_2O_3), is a comparatively weak Raman scatterer, and for this reason serves as a low-interference substrate material. The particle spectrum of Na_2SO_4 (see figure 2 of this report) includes the background spectrum of sapphire, excited with a beam spot of $\sim$2 μm.

The hydroxides of Ca^{2+} and Mg^{2+} were characterized in microparticulate form. $Ca(OH)_2$ was of interest in conjunction with our studies of $CaCO_3$ single particles. The predicted Raman frequencies were observed in the particle spectrum of each compound. Spectroscopic sensitivity for these solid hydroxides extends to particles a few micrometers in size.

Glasses

The matrix of coal fly ash consists primarily of insoluble alumino-silicate glasses, with the surface layers of ash particles generally showing a predominance of certain trace elements.

We have characterized by Raman spectroscopy two types of synthetic glasses which are representative of a series of NBS "standard glasses" of known elemental composition. These glasses have been developed at NBS to serve as elemental standards for quantitative electron probe microanalysis and x-ray fluorescence analysis. They consist in each case of a fused, solid mixture of several oxides. Raman spectra have been obtained from bulk samples (small chips) of two of these glasses. These are identified by their respective composition, in weight percent:

- Glass K-309 (40%, SiO_2, 15% BaO, 15% Al_2O_3, 15% CaO, 15% Fe_2O_3). This material is, in the bulk, an opaque, black glass. In microparticulate form, individual particles are still nearly opaque to transmitted light.

- Glass K-240 (40%, SiO_2, 30% BaO, 5% ZnO, 5% MgO, 10% ZrO_2). This is a clear, honey-colored glass in the bulk. Small particles of it appear totally transparent (colorless) in transmitted light.

In some respects, small particles of these glasses may model the composition and structure (or lack of it) of the solid phase characterizing the "glassy", frequently hollow, spheres found in fly ashes from coal-fired power plants.

The spectroscopic results obtained from measurements on these samples verify the disordered "glassy" structure of these solids.

Our conclusions drawn from a study of these spectra are in agreement with those drawn by others from spectroscopic studies of bulk glasses and various mineral silicates of glass-like structure [4,5,6]. It is a general observation from these studies that the loss of long-range crystalline order in the glass results in very extensive broadening of most spectral features. The vibrational spectrum then is usually indicative of the glassy nature of the sample and often indicates the family of glass (e.g., high or low silica content)

but is much less definitive with respect to the precise composition of the material. Thus, certain of the mineral glasses and glassy solids produced by high temperature reactions may yield well-defined and reasonably intense Raman spectra, whereas others give extremely poor Raman spectra because of the low degree of orderliness in the glass network. It can be generally concluded that the more complex the composition of a glass becomes, the weaker and the more diffuse the Raman bands become. Spectra are then usually flat and featureless; sometimes a sharp band may be identified with included bits of a crystalline phase (e.g., silicate).

These observations have significant implications in regard to the Raman characterization of particulates produced in high temperature zones, such as emissions from coal-fired power plants.

ORGANIC COMPOUNDS AND POLYMERS

It is felt that organic surface layers may exist on power plant emissions. Therefore, the development of techniques for organic micro-Raman analysis is of importance. Spectroscopic measurements have been performed on a variety of solid organic microparticles as well as on polymers, including the following materials:

- Sodium Oxalate, $Na_2C_2O_4$
  Obtained excellent Raman spectra for single particles down to 2 μm in size. An example is shown in Figure 7 of this report.

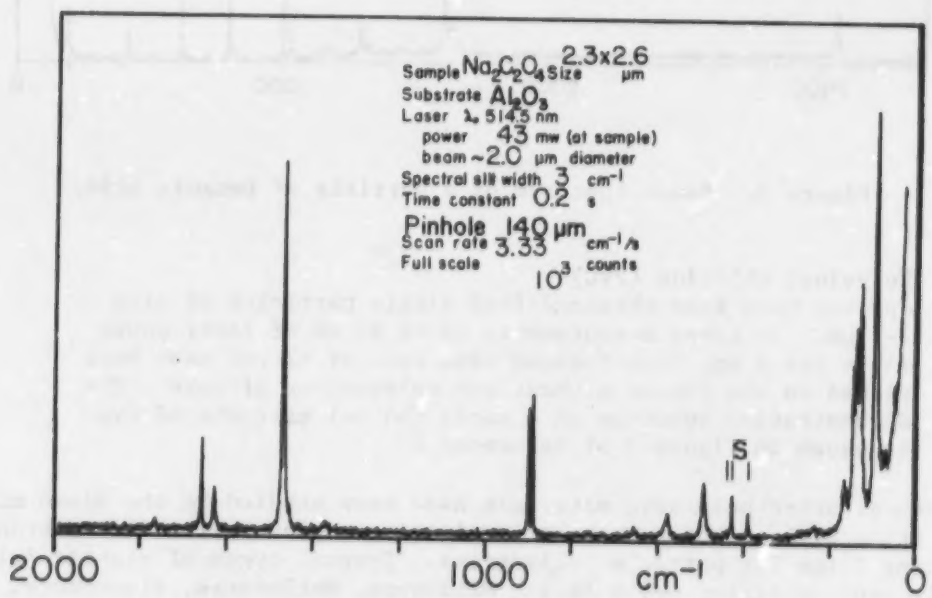


Figure 7. Raman spectrum of a particle of sodium oxalate.

- Urea (carbamide), H_2NCONH_2
  Spectra of excellent signal-to-noise and with good resolution of multiple bands were obtained for particles of size 2-3 μm. These are identical to the reported Raman spectrum of a macro-sample of urea.

- Benzoic Acid, C_6H_5COOH
  Spectra obtained for particles <10 μm in size, requiring low irradiance levels. Typical of these measurements is the spectrum shown in Figure 8, obtained with 10 mW of laser power concentrated in a beam spot of ∿14 μm diameter. Higher irradiance levels (40 mW) have caused slow destruction of the sample as mounted on the LiF substrate. Similar observations have been made for other radiation-sensitive organic particles. Heating of the sample in these cases may be due to the presence of absorbing impurities present in or on the particle.

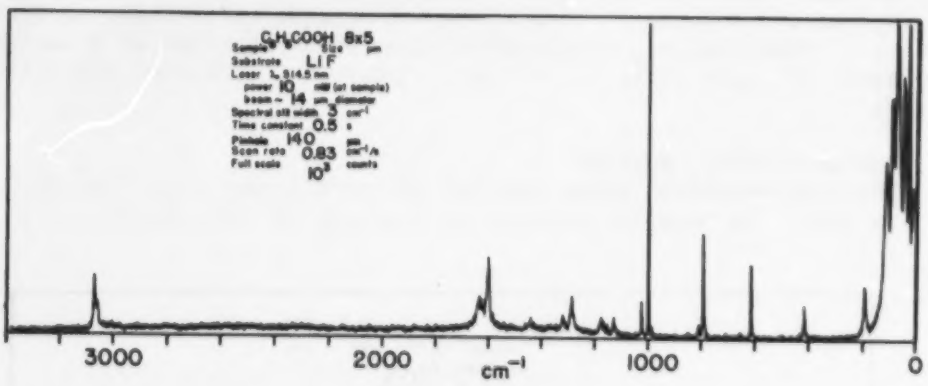


Figure 8. Raman spectrum of a particle of benzoic acid.

- Polyvinyl chloride (PVC)
  Spectra have been obtained from single particles of size 2-7 μm. In these measurements up to 60 mW of laser power (λ_o = 514.5 nm, Beck-focused beam spot of ∿2 μm) have been placed on the sample without any deleterious effects. The demonstration spectrum of a small (∿4 μm) particle of PVC is shown in Figure 7 of Reference 2.

Several other polymeric materials have been studied in the Raman microprobe, primarily for the purpose of evaluating various polymeric membranes as supporting films for particle collections. Several types of plastic films are commonly used as filter media (e.g., Millipore, Nucleopore, Fluoropore, etc.) for the collection of ambient aerosol. These thin, microporous membrane filters (the nominal thickness of 0.8 μm pore size Nucleopore filter is ∿10 μm) are not suitable as supporting films for particles to be analyzed in

the Raman microprobe. For example, membrane filters of the polycarbonate and Teflon variety exhibit fairly complex Raman spectra with intense bands over the entire spectral range of interest. These serious interferences preclude the use of these membranes as substrates and require the removal of particle collections from such filters.

The results obtained to date on organic compounds in microparticulate form are very encouraging and indicate that many of the colorless organics are identifiable in particles down to 1 μm. Limited measurement experience has been gained in the detection and identification of contaminating organic layers on inorganic- or mineral-core particulates. In some cases, organic or biological contaminants present in or on particles have been decomposed — at apparently high induced temperatures — to a carbonaceous residue, as evidenced by the appearance of a pair of broad bands in the 1200-1700 cm^{-1} region of the spectrum. These features, one mode centered near 1350 cm^{-1} and the other around 1600 cm^{-1}, are attributed to a form of activated carbon (or polycrystalline graphite) produced in the thermal decomposition of the organic material.

LIQUID SULFATE AEROSOL

A large number of studies have been conducted by various workers to characterize the properties and identity of atmospheric acid aerosol. In this area of environmental measurement, the emphasis has been on the detection, monitoring and quantitation of several molecular forms of ambient acid aerosol, principally H_2SO_4, NH_4HSO_4 and $(NH_4)_2SO_4$. These species are thought to exist as microdroplets in atmospheric aerosol. Major interest centers on their mechanisms of formation, transformation, dispersal and removal in ambient air. Free (i.e., molecular) H_2SO_4 and NH_4HSO_4 in aerosol form react *in situ* with NH_3 to form $(NH_4)_2SO_4$. Both H_2SO_4 and NH_4HSO_4 are hygroscopic substances which are aqueous solution droplets at all humidities from 30 to 100 percent. In contrast, $(NH_4)_2SO_4$ is a deliquescent salt which undergoes a transition from the dry crystal to a solution droplet at the relative humidity corresponding to that over the saturated solution of the salt (∿80 percent). Thus under normal atmospheric conditions, the latter two forms of acid sulfate may exist in either the solid or the liquid phase.

Because of the significance of the sulfate aerosol system in power plant emissions, we have — in preliminary experiments — applied the Raman microprobe to the characterization of liquid sulfate aerosols. We have attempted to study spectroscopically the transformation from liquid sulfuric acid aerosol to solid, microcrystalline aerosol of ammonium sulfate by reaction with ammonia vapor.

Our experiments have involved the generation of polydisperse sulfuric acid aerosol by nebulization of concentrated sulfuric acid. For micro-Raman investigation, the acid aerosol was collected on the surface of the standard sapphire substrate which, for this application, had been coated with a thin film of a Teflon-like polymer. Initial trials to maintain the spheroidal shape of the aerosol droplets on the uncoated substrate surface failed due to the unfavorable wetting properties of the sapphire. Application of the hydrophobic polymer film provided an impaction surface for the aerosol upon which

droplet shape was maintained for extended periods of time. This also prevented any extensive coalescence of microdroplets.

The transformation from the liquid to the solid aerosol was made by "gas phase titration", exposing the sample to vapors of NH_3 of known concentration (below 100 ppm). Experimental conditions were adjusted to allow for the slow growth of microcrystallites of $(NH_4)_2SO_4$ from the liquid phase. Spectroscopic measurements on single microdroplets were made with the new, expanded beam spot of diameter approximately 7 μm, at full laser power. The size range of the sampled aerosol varied from <35 μm to 2-3 μm. These experiments allowed the spectroscopic detection of undissociated sulfuric acid, H_2SO_4, in microdroplets (down to the size of 5 μm) of the concentrated acid aerosol, the observation of the characteristic Raman bands for the HSO_4^- ion, and the monitoring of the intense Raman line of the SO_4^{2-} ion both in the liquid phase as well as in the solid phase of $(NH_4)_2SO_4$.

Representative results of these very preliminary experiments are shown in Figures 9 and 10 of this report. Prior to reaction with NH_3, the predominant species are undissociated H_2SO_4 and the bisulfate, HSO_4^-, ion. In the spectrum (Fig. 9) of the microdroplet of conc. H_2SO_4 several broad features of low intensity are seen. The Raman shift around 903 cm^{-1} is assigned to the symmetric vibration ν_1 of the H_2SO_4 molecule. In less concentrated solutions (<80 wt%, as is the case here) there exist ionized species, so that the Raman shift centered at 980 cm^{-1} can be assigned to the free SO_4^{2-} ion in solution (c.f. Table 1). The remaining three frequency shifts are characteristic of the HSO_4^- ion in solution, with the band around 1050 cm^{-1} being the strongest of these. The two bands around 420 cm^{-1} and 600 cm^{-1} are primarily due to the bending modes (at 424 and 592 cm^{-1}) of the HSO_4^- ion but also contain the contributions by the ν_2 and ν_4 modes of the free SO_4^{2-} ion (c.f. Table 1).

The transformation from the H_2SO_4 solution phase to the solid phase of $(NH_4)_2SO_4$ is demonstrated by the spectra shown in Figure 10. Measurement parameters were the same as those used to record the spectrum of Figure 9, except for laser power (150 mW) and time constant (0.8 sec). The spectrum (top) of the non-reacted acid droplet displays the features seen in Figure 9. Titration with NH_3 furnishes the "neutralized" droplet, the spectrum (middle) of which is dominated by the sharp, intense 980 cm^{-1} line of the SO_4^{2-} ion in solution. Because of the more complete dissociation of H_2SO_4, this species is now present in much greater concentration, hence the large increase in the strength of the 980 cm^{-1} signal. The broad feature centered around 1100 cm^{-1} arises from the ν_3 mode of the SO_4^{2-} ion. As the transformation is completed and the microparticle is formed, the lower spectrum results, characteristic of crystalline $(NH_4)_2SO_4$. The sulfate symmetric stretch in the solid falls at 976 cm^{-1} and is increased in peak intensity by one order of magnitude. The other bands appear at the expected frequencies (c.f. Table 1).

The significance of these results lies in the capability of the Raman technique to extract species information from <u>liquid</u> microparticles. Considerably more work will be required to assess the present limits of detection (both in terms of droplet size and species concentration) for the various

sulfate forms suspected to be present in atmospheric liquid aerosol. We anticipate that this capability will also be useful to the characterization of liquid aerosol emissions from stationary sources (e.g., oil-fired power plants).

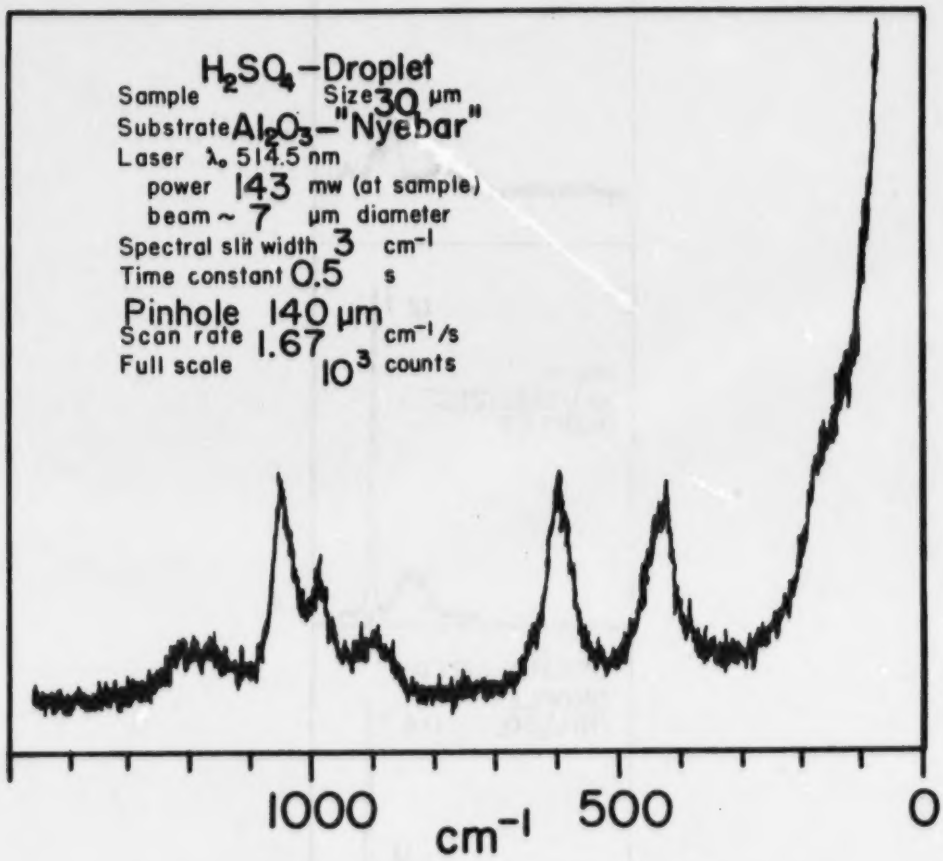


Figure 9. Raman spectrum of a microdroplet of conc. H_2SO_4 supported by a Teflon-coated sapphire substrate.

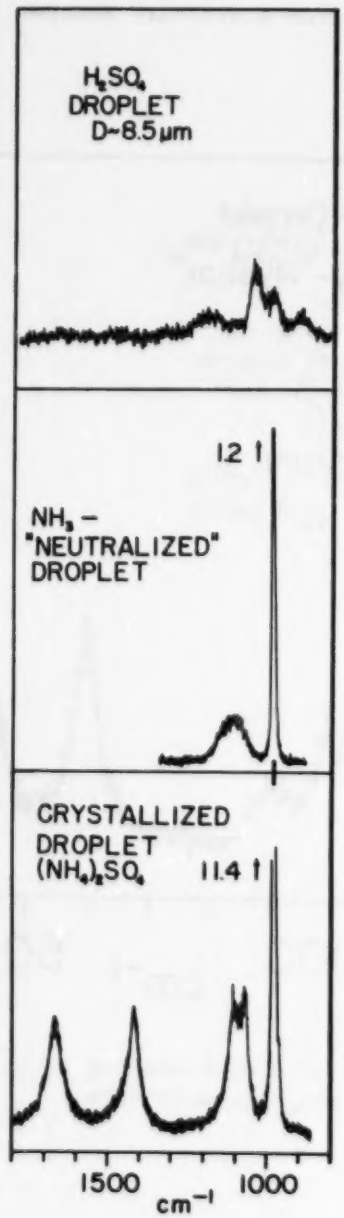


Figure 10. Raman spectra showing the transformation (from top to bottom) from a microdroplet of conc. H_2SO_4 to a microparticle of $(NH_4)_2SO_4$ on reaction with ammonia.

SECTION 6

CHARACTERIZATION OF UNKNOWN PARTICLES FROM POWER PLANT EMISSIONS

With the emphasis on the need to control emissions from stationary sources there arises the need for more information on the composition of fly ash particles emitted into the atmosphere. Coal- and oil-fired power plants are among the largest anthropogenic point sources of particulate matter.

Limited knowledge is available from bulk samples on the relationship between particle size distribution and composition in power plant emissions. On a particle-to-particle basis there exists no information on the molecular identity of these particulates.

The project objectives include feasibility studies on the micro-Raman characterization of air pollution particles caused by the combustion of fossil fuels, especially a study of the identity of combustion-produced (sulfate) acid aerosol in emissions from oil-fired power plants. The primary interest centers on the identity of the molecular states of oxygenated sulfur-containing species that are believed to be closely associated with the particulate carbon (i.e., soot) in these samples. Preliminary studies have been undertaken in this area of stationary source emissions characterization, and the results of these measurements are summarized in the following.

FLY ASH FROM COAL-FIRED POWER PLANTS

Exploratory micro-Raman measurements were carried out on single fly-ash particles contained in NBS Standard Reference Material, Coal Fly Ash, SRM 1633 ("Trace Elements in Coal Fly Ash"). The bulk ash is a sieved (<88 μm) and blended material collected by electrostatic precipitators.

Fly ash particles generally in the size range 5-20 μm were examined in the Raman microprobe, employing high irradiance levels placed on the sample with the Beck-focused ∿2 μm beam spot. The majority of the particles analyzed exhibited weak and diffuse spectra, often with high background levels merging into the broad wing of the Rayleigh line. In a small number of cases, that is for particles so far unidentified, the spectrum shows a broad band at around 450 cm^{-1}, accompanied by a second broad feature at around 950 cm^{-1}, indicative of a glass-like structure and perhaps evidence of Si-O stretching vibration. For a number of large (10-20 μm) irregularly-shaped particles, a very strong, sharp band has been observed at 470 cm^{-1}, in addition to a broad band of medium intensity at 205 cm^{-1} and a very sharp intense band at 128 cm^{-1}. Collectively these features are indicative of crystalline quartz (α-SiO_2).

The lack of strong Raman scattering observed for most of the particles analyzed may also be explained by the fact that in these cases they may be hollow spheres.

Coal fly ash sample #DPC 15A is a bulk sample of fly ash made available for micro-Raman study by the EPA. The sample is an in-stack sample, collected after precipitators; received in the form of a heavy, dense layer of particulate deposit on a 80 mm diameter glass fiber filter. A micro-Raman sample (using a LiF substrate) was prepared by transferring a light brushing of the ash deposit onto the substrate. Examination of this preparaton in the polarizing light microscope at magnifications from 50-625X showed that the ash consisted of a distribution of very fine, spherical particles, all of which are <2-3 μm in diameter. The majority of the particles in this ash proved to be around 1 μm in size and smaller, appearing in the form of extensive clusters and chains in the sample prepared for Raman analysis. Only a small fraction of the ash particles existed in this preparation as discrete particles. Individual fly ash spheres or clusters of particles showed little or no birefringence. They appeared fairly transparent (although difficult to judge because of their small size) in transmitted light and showed various hues of color (mainly shades of brown and green). Spectroscopic measurements were made with 514.5 nm excitation (i.e., green line of Ar^+/Kr laser) employing a range of irradiance levels. The lowest practical irradiance levels (on the order of kilowatts/cm^2) placed on the sample produced heating in the particles probed by the beam, as was evident from the spectral response. In these cases the spectra show high background signal levels (due to broad-band non-Raman emissions from the sample) that usually completely swamp any Raman event. Frequently these high, interfering light levels decay with time and continued irradiation of the particle. Moderate to high irradiance levels placed on these ash particles have had the effect of decomposing, melting, and vaporizing a fraction or all of the irradiated sample. In cases where a larger beam spot (7-15 μm in diam.) was placed on a cluster of particles, this interaction has brought about the fusion of these particle aggregates into large spheres or globs of solid material. Residue spheres of this type have been produced with diameters 20-30 μm. We attribute the excessive heating of these particles to the presence of constituents effectively absorbing the energy at the excitation frequency. These may be various colored metal oxides in the matrix or on the surfaces of the particles or, in fact, films of combustion-produced carbon.

Further research is required in the study of such samples. Certain advantages might be gained, for example, from the use of other excitation frequencies. These have not been explored in our work. Other output frequencies (e.g., 488.0 nm blue and 676.4 nm red) are available from the laser at adequate power levels but have not been employed in the routine measurements described here. As is typical of all Raman spectroscopic analyses of colored samples, some advantages can be gained from the use of other frequencies. The choice of a "best" excitation frequency is complicated by such factors as heating from absorption of the exciting beam, fluorescence from the sample and possible resonance effects. For unknown samples it is difficult to *a priori* select the optimum excitation frequency, and only after experience is gained for each measurement problem can the "best" excitation be chosen.

PARTICULATE EMISSIONS FROM OIL-FIRED POWER PLANTS

Various EPA particle samples of oil-fired power plant emissions have been received for micro-Raman analysis.

In the time available for the application of the technique to the characterization of these samples, we have focused our efforts on a preliminary study of a set of samples from an oil-fired power plant designated as Site A by EPA. These samples were sent to NBS in the early part of September 1976.

This set of five samples was collected by the sampling staff of the Stationary Source Emissions Research Branch of the EPA/RTP, at the Site A power plant on August 19, 1976. Sample collection involved the use of a five-stage Battelle cascade impactor in the out-stack sampling mode. Sampling was conducted at the fourth port from the bottom, stack temperature was 325 °F (163 °C). The sampler was positioned at the end of a 8ft.-long sampling train (i.e. probe of ½" I.D.), with the probe and sampler heated to 200 °F (94 °C).

On each of the five stages the impactor employed a micro-Raman substrate to collect the size-fractionated aerosol. Only on the third stage was a substrate used bearing an aluminum film particle finder grid.

The power plant at Site A is operated without emission controls. During the test, the unit was operated at an excess boiler oxygen level of about 0.2 percent, using a fuel of sulfur content 2.5 percent with concentrations of vanadium about 400 ppm.

The particulate emissions from the plant at Site A have recently been characterized by EPA investigations [7,8]. These studies have included the determination of particulate mass, particle size distribution and trace element composition from bulk collections obtained by in-stack and out-stack sampling methods. Elemental analysis by x-ray fluorescence shows compounds of sulfur, vanadium and nickel to be major components in these particulate emissions samples. The molecular form of these compounds (e.g., oxides, sulfates, vanadates, etc.) cannot be inferred from this data on the trace element composition. The carbon content of these samples is found to be typically 60 wt. percent. Thus, these samples as collected in the bulk (e.g., as deposits on filters) have the appearance of finely-divided black powder. Exposed to the ambient air, such particulate samples are believed to take up enough moisture to form appreciable amounts of "acid smut" (i.e., a mixture of hygroscopic acid aerosol and carbon).

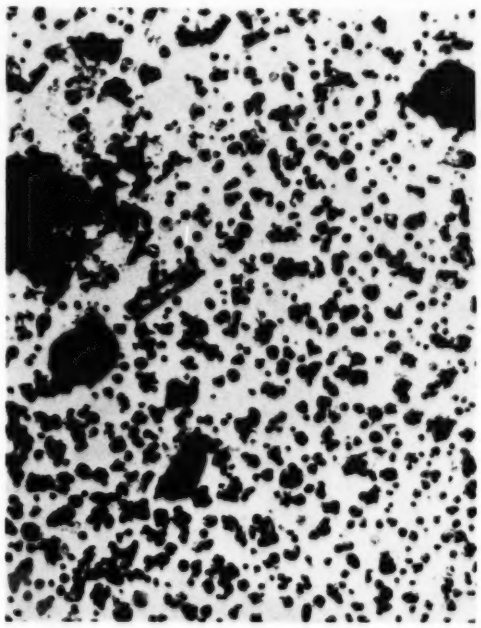
Characterization by Light Microscopy

Microscopic investigation of the set of five Site A emissions samples was made with a research microscope with photomicrographic camera. All observations were made in transmitted light, at various magnifications from 50X to 625X. The object was to take note of the optical properties and morphology of the particles collected on each stage and to record their location on the substrate for subsequent micro-Raman analysis.

In Figures 11 through 14 are given selected optical micrographs showing representative fields of view of the particle deposits on each of the five sample substrates. The substrate is in all cases the usual optical-quality sapphire. On stage 3 the sapphire had deposited on it a thin aluminum film in the design of a particle finder grid. Figure 11 shows the particulate material collected on stages 1 and 2 of the sampler. On these stages, as on the others, the sampled particulate material ranges from colorless to pale yellow, orange, light brown, greenish brown, brownish red and black. Figure 12 shows representative areas of the stage 3 sapphire substrate where the impacted aerosol (apparently solid and liquid) has reacted with the thin aluminum film. What is seen, therefore, in the aluminized areas are predominantly the reaction products. Vast areas of the grid are destroyed and have been etched away as a result of the chemical interaction that has taken place. Careful microscopic examination of this stage shows liquidus or deliquescent microparticulates and a multitude of microcrystallites of various colors, reminiscent of dendritic growth. In Figure 13 are shown selected photomicrographs of the emissions collected on stage 4. The low-magnification (50X) photo shows the central area of the substrate, with several large (>100 μm) dendrite type crystals in a field of black, spongy particles or aggregates. The predominant, four-leaf crystal shown at 125X and 312X magnification is about 200 μm in size. Very interesting are also the many groupings of micro-dendrites on this stage, of which a typical one is shown (at 312X) in the fourth micrograph of Figure 13. It appears that these microcrystals have grown on the substrate, presumably from the reaction of various combustion products present in all phases of matter. As of this time, micro-Raman measurements have only been made on selected particles of stage 4. An overview of the sampled aerosol collected on stage 5 is given in Figure 14. The 50X micrograph shows splays of fluid collected at the periphery of the substrate, with ensembles of microcrystallites entrapped in transparent, solid "skins". The center of the sample, presumably the area of most direct, hard impaction, is shown at 125X featuring carbonaceous, spongy material and films or sheets of solid, colored material. The two higher magnification (312X) photos show extensive liquidus material, in microdroplets of all sizes. Particularly interesting is the colony of microcrystals seen in the fourth micrograph. The origin and formation of these features is unexplained.

Results of Micro-Raman Analysis

Exploratory spectroscopic measurements have been made on particles collected on the Raman substrate of stage 4. In these studies spectra could be obtained from particles that did not show any intense coloration and appeared to be relatively free from fine particulate soot. Basically three representative types of particulates have been probed in this sample. Predominant on this stage are several large and many smaller dendrite crystals grown on the substrate (i.e., sapphire) surface. A number of these microcrystals (c.f. Fig. 13) have been analyzed in the Raman microprobe. The second major type consists of particles of varying size and shape close to the brown microcrystals described above. These particles are mostly globular, do not appear to be porous, but seem to be a compact, fused mass of crystalline material, with various degrees of transparency. Spectroscopic analysis indicates that these particles are inhomogeneous in composition. They seem to be made up of a colorless, transparent solid material interspersed with other solid material



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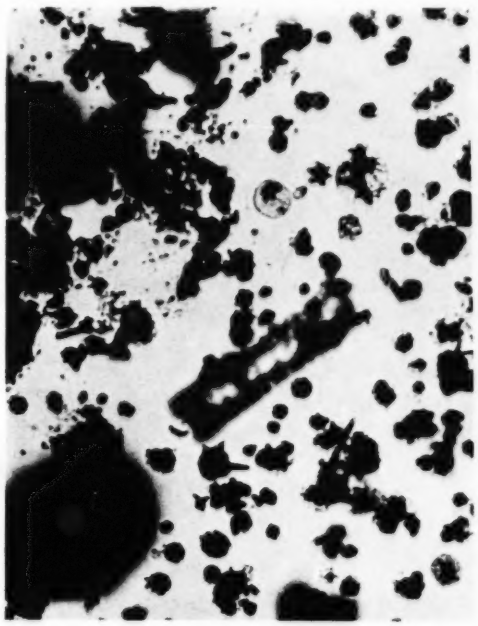

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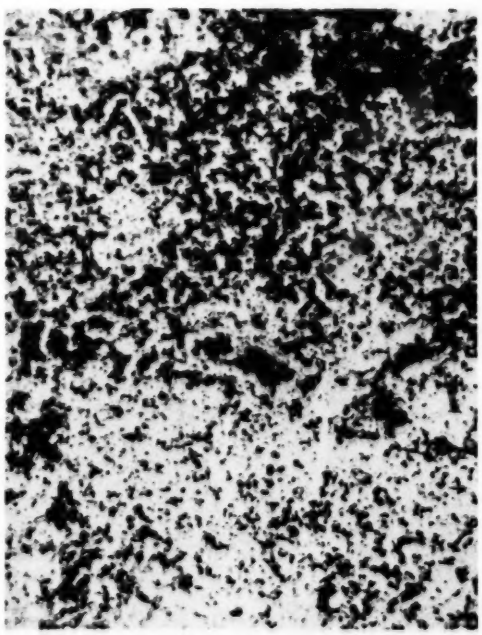

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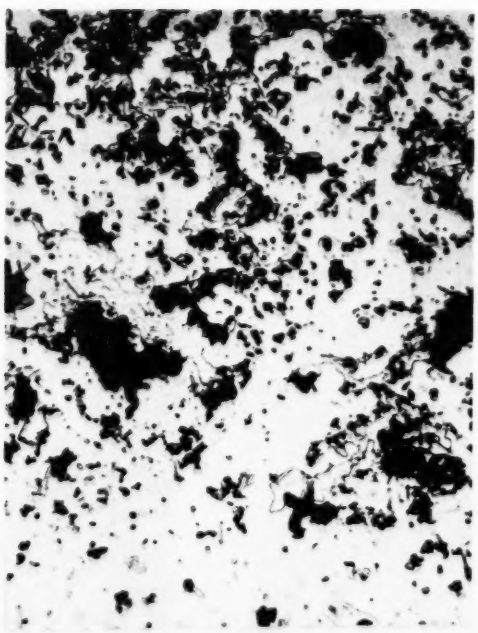

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Figure 11. Optical micrographs of Site A power plant particulate emissions collected on stages 1 and 2 of Battelle impaction sampler.

50X

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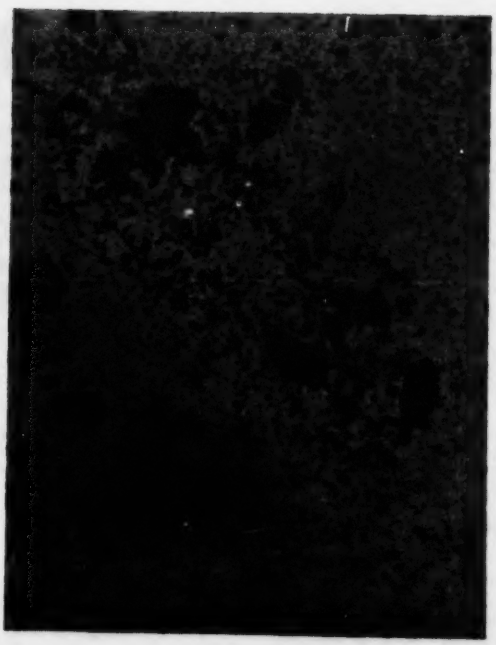

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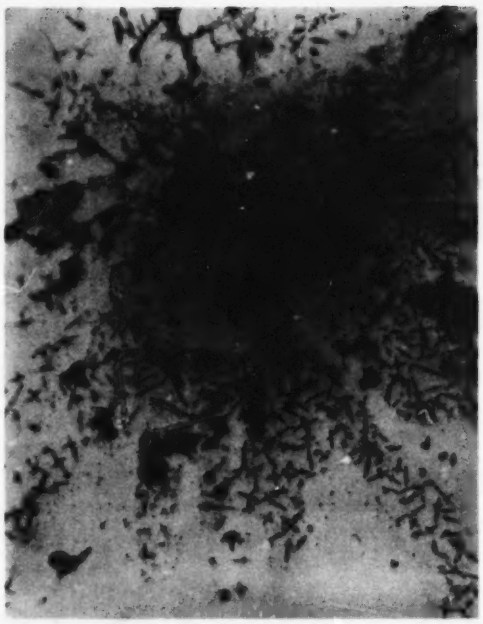
Figure 12. Optical micrographs of Site A power plant particulate emissions collected on stage 3 of Battelle impaction sampler.



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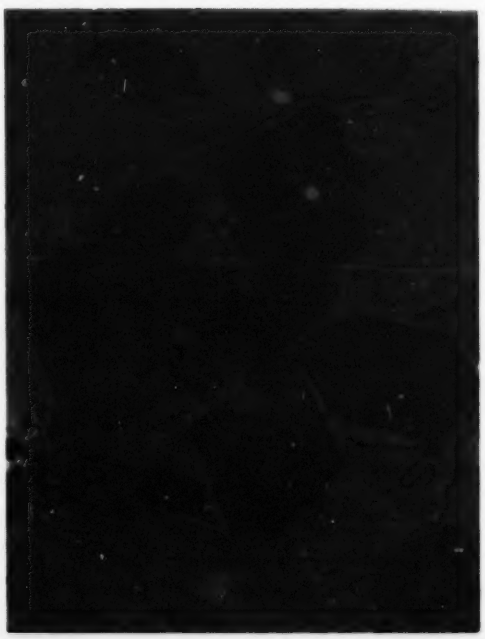

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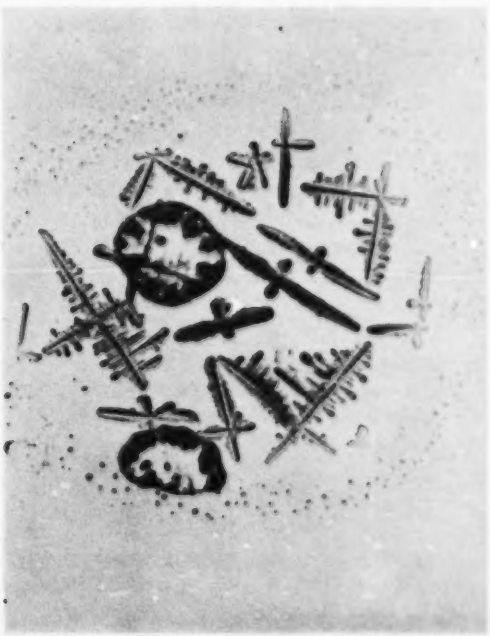

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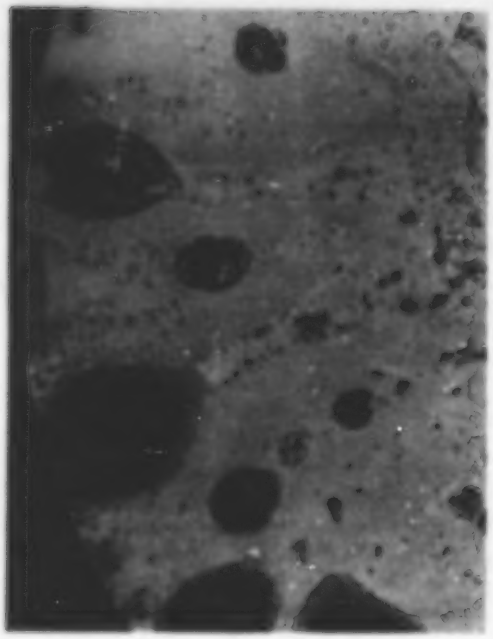
Figure 13. Optical micrographs of Site A power plant particulate emissions collected on stage 4 of Battelle impaction sampler.



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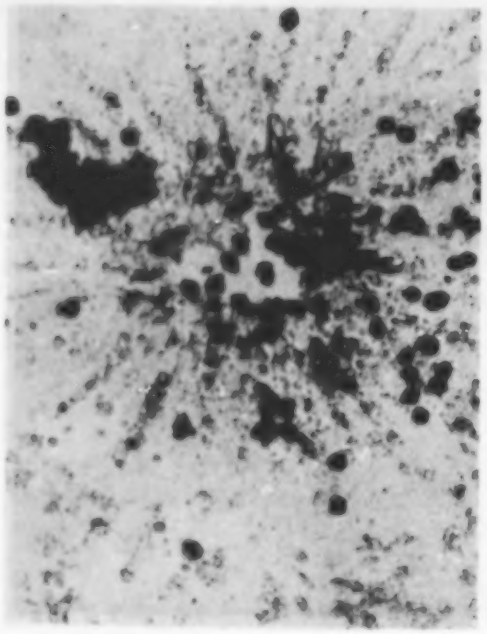

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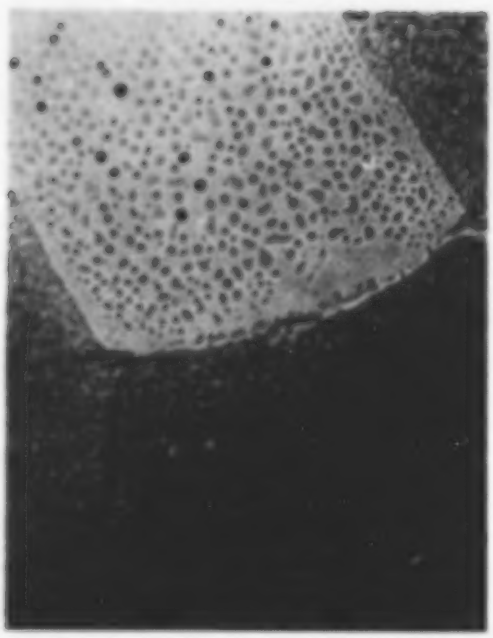

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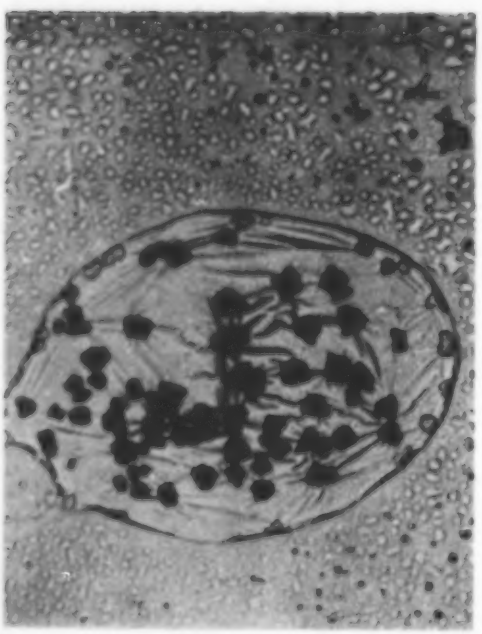

312X

Figure 14. Optical micrographs of Site A power plant particulate emissions collected on stage 5 of Battelle impaction sampler.

varying in color from shades of brown to green, with bits of black material included. This second class of particles has also been analyzed spectroscopically, and Raman spectra have been obtained which are discussed below. A third type appears as colorless, transparent strands, connecting the two types of particulates described above. These thin strands, and frequently sheets, of colorless, deposited material have also been analyzed.

Our measurements of several particulates on the fourth impactor stage have furnished a number of essentially identical Raman spectra for the dendrite type microcrystals. Representative of these spectra is that shown in Figure 15, obtained from probing a small segment of the large, four-leaf crystal (c.f. optical micrographs shown in Figure 13). The predominant features in these spectra are bands with Raman shifts around 145, 280 and 1000 cm^{-1}. We have performed additional measurements on several other microcrystals of this type, type, including small dendrites (c.f. 312X micrograph of Figure 13) of size down to 5 μm. From these studies we have obtained spectra consistent with the earlier ones. As a result of further characterization of known compounds, we have since been successful in interpreting the observed Raman spectra. The

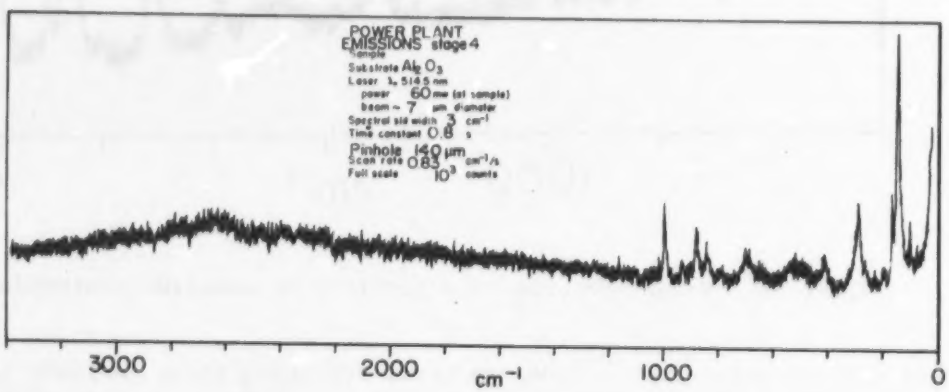

Figure 15. Micro-Raman spectrum of a large microcrystal (shown at 312X in Figure 13) found on stage 4 of the sampled power plant emissions (see text).

major constituent present in these particles is crystalline vanadium pentoxide, V_2O_5. This is indicated from a comparison of the reference spectrum of a small (4x5 μm) particle of V_2O_5, — shown in Figure 16 —, with the spectrum of the unknown microcrystal shown in Figure 15. The vibrational Raman spectrum of crystalline V_2O_5 has been discussed in the literature [9]. The bands that are nicely resolved in the spectrum of the microparticle have frequency shifts 104, 144, 285, 406, 701 and 995 cm^{-1}. These same bands are observed with equally good resolution in the spectra of the unknown microcrystals. There exist, however, additional bands of medium intensity, — in the region 820 to 970 cm^{-1}, — which are absent in the spectrum of pure V_2O_5. At this time we cannot

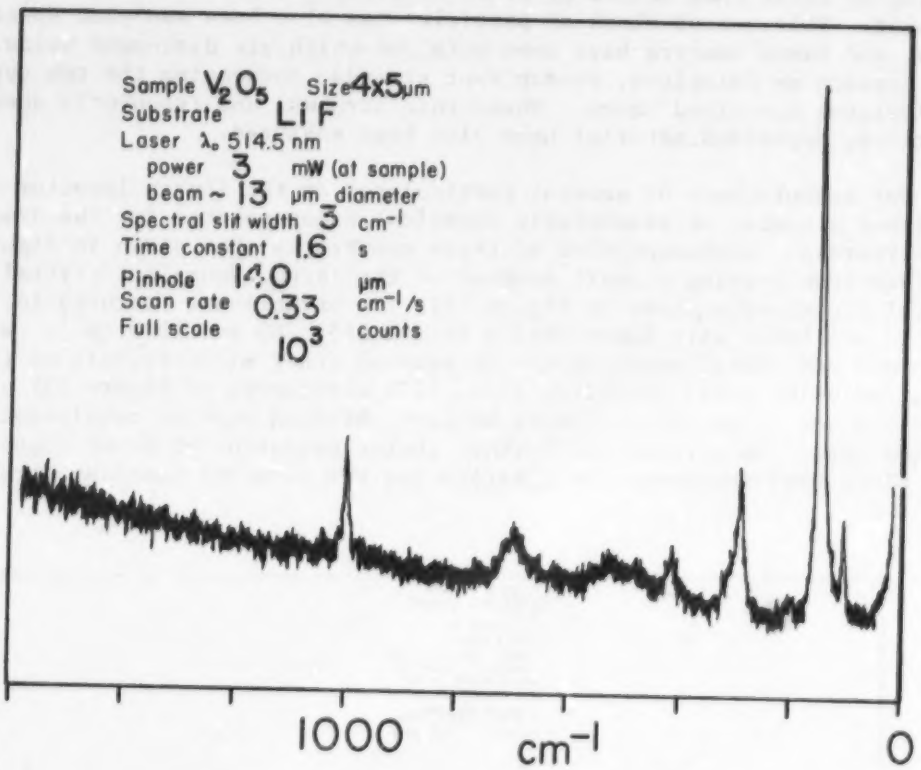

Figure 16. Raman spectrum of a particle of vanadium pentoxide.

account for the existence of these spectral features; these indicate the presence of a second component which we have not detected in the spectra of the other two types of particulates which we have analyzed. In parallel with our study of V_2O_5 we have also examined the spectra of microparticles of reagent-grade, crystalline vanadyl sulfate, $VOSO_4 \cdot 2H_2O$, [10]. The spectrum of a small particle of this salt just under 10 μm in size, is shown in Figure 17. Infrared data for this salt have been reported [10], but Raman data do not appear to exist. The most intense band in the spectrum is the ν_1 symmetric S-O stretch of the sulfate ion falling at $\sim$1010 cm^{-1}. Two other sharp bands of strong intensity appear at higher frequencies of the ν_1 fundamental mode. In addition, several well-resolved, sharp bands are seen in the low frequency (<400 cm^{-1}) region which may be attributed to various V-O vibrations and lattice (or external) modes of the crystal. None of the bands characteristic of $VOSO_4$ are present in the spectra of the unknown microcrystals (c.f. Figure 15). We therefore feel that the vanadium present in these particles does not exist in the form of the vanadyl ion, VO^{2+}, but appears to essentially exist in the +5 oxidation state (as in V_2O_5). Other oxides of vanadium such as V_2O_3 and V_2O_4 are known to exist and are formed by oxidation of vanadium. Since no spectral data exist for these species it is not clear whether the

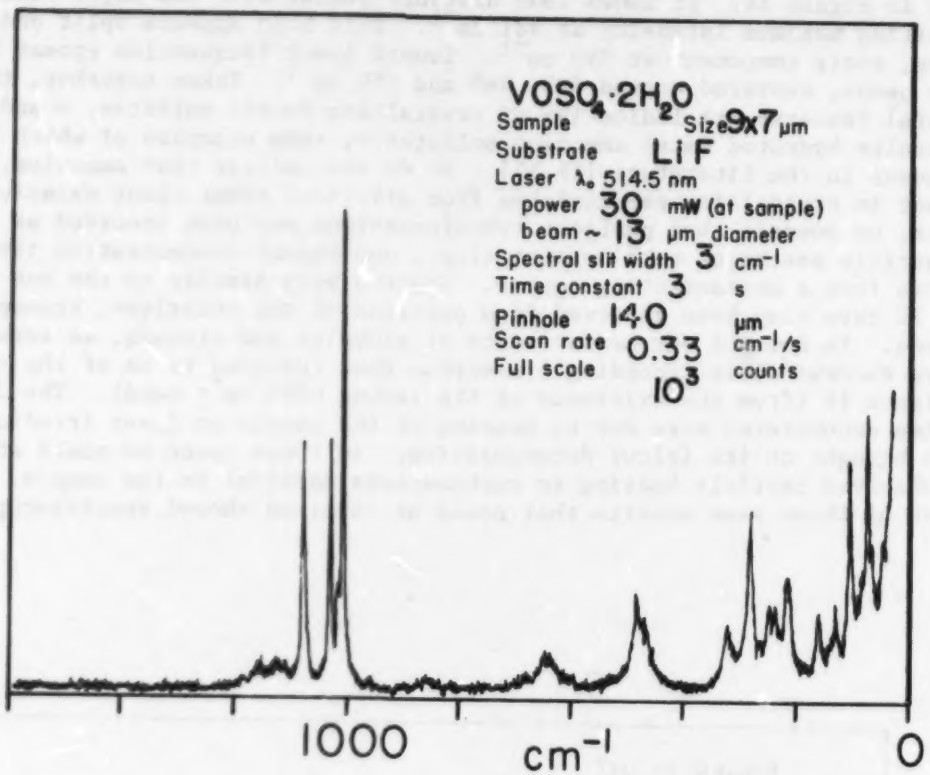

Figure 17. Raman spectrum of a particle of vanadyl sulfate.

features in the 820 to 970 cm^{-1} region are due to these possible lower oxides. We have also considered the vibrational spectroscopy of the (ortho-) vanadate ion, VO_4^{3-}, – also containing pentavalent vanadium –, and are inclined to conclude that the existence of this species is not indicated in the spectra we have recorded from these particles. The vanadate anion is tetrahedral as are PO_4^{3-} and SO_4^{2-}, therefore four fundamental modes are expected to be active in the Raman. For the "free" vanadate ion, these internal vibrational modes are observed [4] at Raman shifts 827 (ν_1), 341 (ν_2), 780 (ν_3) and 341 cm^{-1} (ν_4). Raman data on crystalline vanadates (including the meta-vanadate ion, VO_3^-) seem to be non-existent in the literature. For this reason, we have begun to study the spectroscopy of some of these solids (e.g., KVO_3, Na_3VO_4). Various other microcrystals in the specimen have yielded Raman spectra in full agreement with the spectrum obtained for V_2O_5 (c.f. Figure 16). In these cases, the additional spectral features seen in the region 820 to 970 cm^{-1} are absent, and it can be concluded that these crystals consist of the oxide essentially free from any other second component.

In addition, we have obtained a second type of Raman spectrum from the globular type of particulates described earlier which indicates the presence of a crystalline sulfate. Representative of these results is the spectrum

shown in Figure 18. It shows four distinct peaks, with the major band exhibiting maximum intensity at 981 cm^{-1}. This band appears split and has a second, sharp component at 990 cm^{-1}. Toward lower frequencies appear three other bands, centered around 625, 460 and 150 cm^{-1}. Taken together, these spectral features are indicative of crystalline double sulfates, – and in particular hydrated metal ammonium sulfates –, some examples of which have been discussed in the literature [11,12]. We do not believe that ammonium, NH_4^+, is present in crystalline particulates from oil-fired power plant emissions. Rather, we suspect that particle transformations may have occurred as a result of particle reactions with ambient (i.e., non-stack) concentration levels of ammonia from a contaminating source. Spectra very similar to the one shown in Fig. 18 have also been observed from portions of the colorless, transparent strands. In some of our measurements of globules and strands, we were not always successful in recording a spectrum that appeared to be of the type shown in Figure 18 (from the existence of the strong ∿980 cm^{-1} band). The difficulties encountered were due to heating of the sample on laser irradiation which brought on its (slow) decomposition. In these cases we could attribute the observed particle heating to carbonaceous material in the sample. A number of these same spectra that could be obtained showed spectroscopic

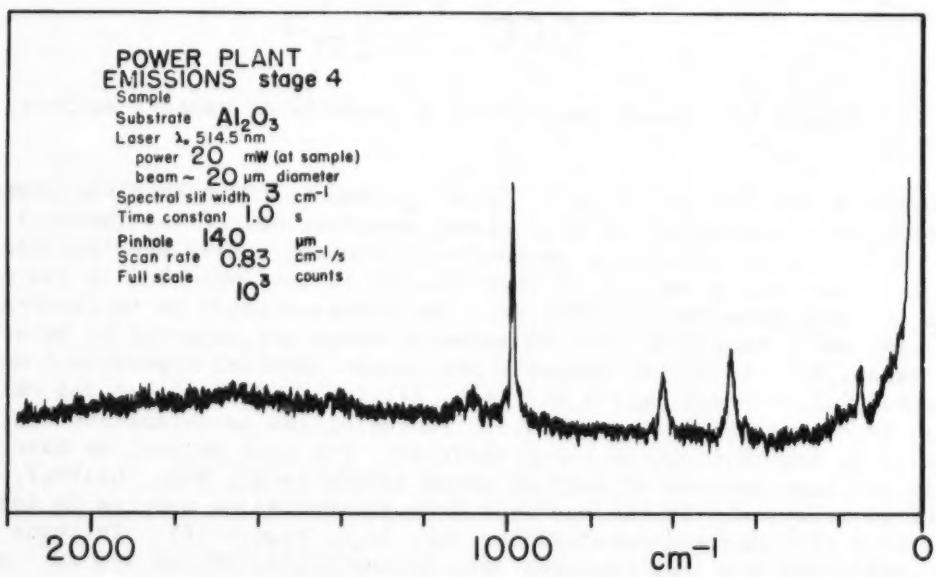

Figure 18. Raman spectrum of a globular particle found on stage 4 of the sampled power plant emissions.

evidence for the presence of a carbonaceous residue. We are familiar with the appearance of "carbon bands" in the spectra of environmental particles from our measurements on urban air particulate dusts. An example is shown in Figure 19. The major constituent of this small particle is calcite, $CaCO_3$ [13]. Present also is a small quantity of anhydrite, $CaSO_4$, — evident from the medium intensity band at $\sim$1020 cm^{-1} —; a pair of distinct, well-defined bands attributable to carbon is observed with the two maxima centered around 1350 cm^{-1} and 1580 cm^{-1}. These same features have appeared superimposed upon the spectrum of Figure 18 for several of the emissions particulates we have analyzed. Bands very similar in shape and peak frequency have been observed from pure, polycrystalline graphite [14]. We can suggest two possible explanations for the appearance of carbon bands in the spectra of urban dust particles and power plant particulate emissions. One would be that they arise from combustion-produced carbon (e.g., soot) associated with such samples. On the other hand, we cannot exclude the possibility that these bands may derive from laser-induced thermal decomposition of organic components (e.g., oil films). The first rationale is in agreement with the observations made by other workers in the study (by ESCA methods and laser Raman spectroscopy) of carbon associated with bulk samples of atmospheric particulates [15]. We are presently conducting experiments with the intent to study spectroscopically the creation or evolution of these carbon bands in the analysis of microparticles intentionally contaminated with polycrystalline carbon films or with surface layers of polycyclic organic compounds of the type suspected [8] to exist with oil-fired power plant emissions.

We intend to continue our measurements of the Site A particle samples and plan to also perform electron-probe analyses on particles measured in the micro-Raman spectrometer. The characterization of known materials will continue as an important activity so as to increase the reference data base for molecular identification of unknowns. Based on our preliminary results obtained in the study of liquid aerosol microdroplets, we hope to be able to extract useful spectroscopic information from the liquid material collected on stage 5 of the sampler (c.f. Figure 14).

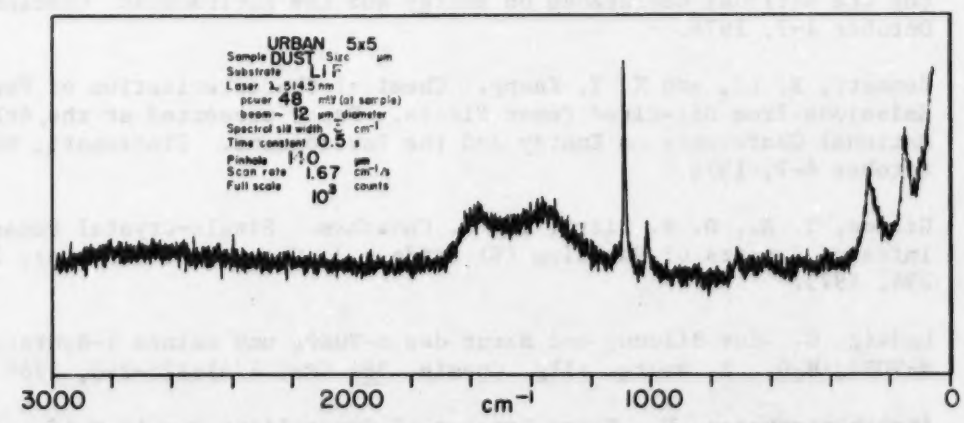

Figure 19. Raman spectrum of a particle of calcite ($CaCO_3$) in urban air particulate dust.

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